

Thermal Diffusivity and Oxidation of 2D and 3D C/SiC Composites from 600°C to 1400°C

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ABSTRACT

A 2D C/SiC and a 3D C/SiC composite were prepared by a low-pressure chemical vapor infiltration method. Thermal diffusivity of the composites was measured in a mixed gas flow of O₂ and Ar that was used to simulate air. The thermal diffusivity change and the weight change with oxidation time at temperatures from 600°C to 1400°C were investigated. The thermal diffusivity of 2D C/SiC was higher than that of 3D C/SiC over the entire temperature range. The former was more sensitive to oxidation than the latter. Below 1000°C, the thermal diffusivity of 2D C/SiC decreased with increasing oxidation time. The lower the temperature, the more rapidly it decreased. There was no clear decrease in the thermal diffusivity of 3D C/SiC with increasing oxidation time in the whole temperature range. At 600°C, the weight loss of both composites was accelerated in a parabolic relation to oxidation time, but their thermal diffusivity decreased linearly. At 1300°C, the weight loss of both composites was decelerated in a parabolic relation to oxidation time, but no obvious thermal diffusivity change corresponded to the weight loss. Therefore, oxidation affected much more strongly the weight loss than the thermal diffusivity of C/SiC composites.

Key Words: Carbon composites, oxidation, thermal diffusivity

1. INTRODUCTION

Carbon fiber reinforced silicon carbide composites (C/SiC) were developed and tested for thermostructural applications, such as components of turbine engines, the reentry thermal protection system of spacecraft, ultra-lightweight mirrors and so on [1,2]. Thermal diffusivity is one of the most important properties for all these applications. Of the two main kinds of C/SiC composites, 2D C/SiC is more often used to fabricate components such as plates, tubes and shells, and 3D C/SiC is used more to fabricate components such as nozzles.

Although the same four constituents, SiC matrix, PyC interlayer, fibers and pores, are included in 2D and 3D C/SiC composites, their microstructure is different. Three interesting problems arise in this connection. Firstly, 2D and 3D C/SiC composites will have different thermal diffusivities because this property is sensitive to microstructure. Secondly, they will have different oxidation resistances due to different thermal mismatch between the fibers and the SiC matrix. Thirdly, they will have different thermal diffusivity changes with oxidation time owing to different oxidation resistances. By answering these problems it will be possible to clarify how much the SiC matrix deposited in different performs affects the thermal diffusivity, which is the controlling property, and whether it can be used as a property for evaluating damage of the composites during service. These are very important for applications of C/SiC composites.

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Thermal diffusivity of 2D and 3D C/SiC composites has been investigated and a few data can be found in the literature [3], but the effect of oxidation on the thermal diffusivity has not been reported. In this article, 2D and 3D C/SiC composites were prepared, and the thermal diffusivity and the weight change of the composites with oxidation time in an oxidizing atmosphere at different temperatures were investigated.

2. EXPERIMENTAL PROCEDURE

2.1. Fabrication of the specimens

Three-dimensional (3D) performs were braided by a four-step method, and two-dimensional (2D) performs were laminated by laying up carbon fabric with the volume fraction of fibers being controlled in the range from 40% to 45%. These two kinds of performs were deposited with pyrolysis carbon (PyC) and SiC, using butane and methyltrichlorosilane (MTS). The deposition conditions of the PyC interlayer were as follows: temperature 960°C, pressure 5kPa, time 20 hours, Ar flow 200 ml·min⁻¹, butane flow 15 ml·min⁻¹. The deposition conditions of SiC matrix were as follows: temperature 1000°C, pressure 5kPa, time 120 hours, H₂ flow 350 ml·min⁻¹, Ar flow 350 ml·min⁻¹, and the molar ratio of H₂ to MTS 10. A CVD SiC coating was applied to the prepared 2D and 3D C/SiC specimens after machining under the same conditions as the SiC matrix.

2.2. Oxidation and thermal diffusivity change

The Laser Flash Apparatus LFA 427, made by the Netzsch company, was employed for measurements of the thermal diffusivity. The required specimen size was $\phi 12.5 \times 2 \text{ mm}^2$. All measurements were conducted in a mixed gas flow of O₂ and Ar that was used to simulate air at different temperatures from 600°C to 1400°C. The thermal diffusivity was measured every 10 minutes during six hours, and the weight change was measured after oxidation for three and six hours, respectively.

3. RESULTS AND DISCUSSION

3.1. Thermal diffusivity change with oxidation time

The thermal diffusivity of 2D C/SiC as a function of

temperature is compared with that of 3D C/SiC in Fig. 1. The thermal diffusivity of both composites decreased rapidly with increasing temperature below 1000°C and did not change significantly above 1000°C. The thermal diffusivity changes of 2D C/SiC with oxidation time at different temperatures are shown in Fig. 2. The thermal diffusivity changes below 1000°C were plotted as black circles and those above 1000°C were plotted as open circles. It can be seen that the former were lower than the latter. Below 1000°C, the thermal diffusivity decreased linearly with increasing oxidation time. The lower the temperature, the more rapidly it decreased from 600°C to 1000°C. This indicated that the thermal diffusivity of 2D C/SiC at a low temperature was more sensitive to oxidation than at a high temperature due to

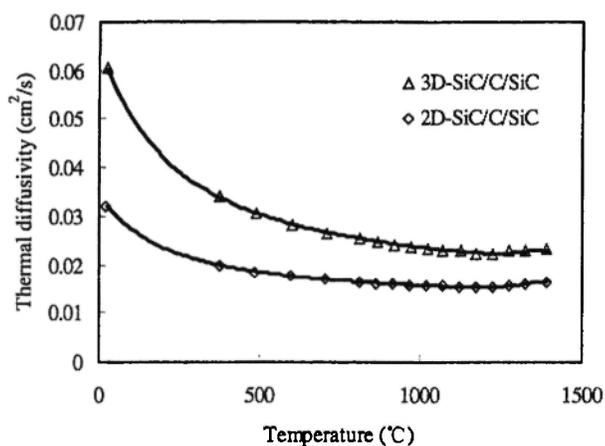


Fig. 1: Relation of thermal diffusivity of 2D and 3D C/SiC to temperature

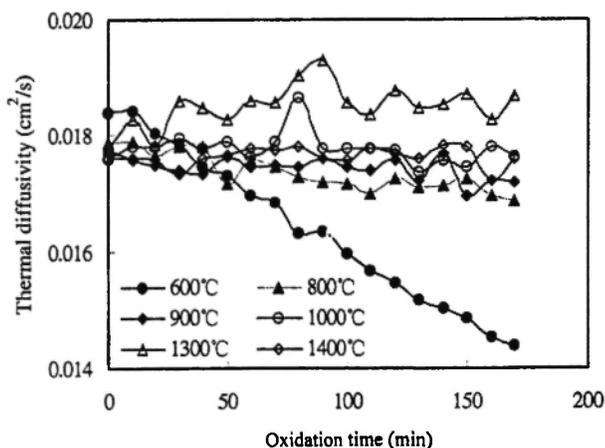


Fig. 2: Thermal diffusivity changes of 2D C/SiC against oxidation time at different temperatures

uniform oxidation of the carbon phase in three hours. Above 1000°C, the thermal diffusivity did not decrease significantly, although it fluctuated intensively. This is considered to be produced by non-uniform oxidation of the carbon phase and the formation of silica, the former decreasing and the latter increasing the thermal diffusivity.

The thermal diffusivity changes of 3D C/SiC with oxidation time at different temperatures are shown in Fig. 3. It can be seen that the thermal diffusivity of 3D C/SiC was not sensitive to oxidation over the entire temperature range although it decreased slightly with increasing oxidation time below 1000°C. The thermal diffusivity decrease with increasing temperature was irregular because the difference produced by using different specimens was greater.

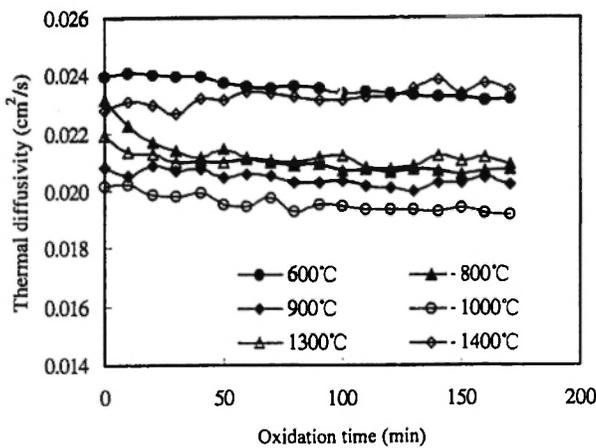


Fig. 3: Thermal diffusivity change of 3D C/SiC against oxidation time at different temperatures

The weight changes of 2D C/SiC and 3D C/SiC after oxidation at different temperatures for three hours are shown in Fig. 4. The weight change of 3D C/SiC was greater than that of 2D C/SiC below 1000°C, but the thermal diffusivity of the former decreased much more slowly than that of the latter. It can be concluded that the thermal diffusivity of 3D C/SiC was controlled mainly by the SiC matrix which was controlled by cooperation of the SiC matrix and the carbon phase. The different mechanisms should be related to different distributions of the SiC matrix in these two composites. The carbon phase had an obvious effect on the thermal

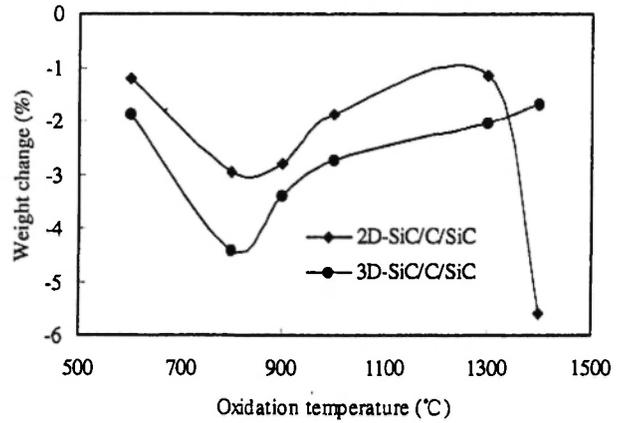


Fig. 4: Weight changes of 2D and 3D C/SiC after oxidation for 3 hours at different temperatures

diffusivity of 2D C/SiC because most of the SiC matrix was deposited in laminated pores. Most of the SiC matrix was deposited in the well-distributed pores between bundles, and then the thermal diffusivity of 3D C/SiC was not affected by the carbon phase.

The weight change of 2D C/SiC was much greater than that of 3D C/SiC at 1400°C, but the thermal diffusivity of the two composites did not decrease. The carbon phase was only oxidized in some areas where non-uniform oxidation took place above 1000°C, and then the thermal diffusivity was not sensitive to oxidation during three hours.

3.2. Thermal diffusivity and weight change at 600°C

Figure 5 shows the relation between the thermal diffusivity and weight change of 2D C/SiC and the oxidation time at 600°C. The weight loss accelerated parabolically with increasing oxidation time, but the corresponding thermal diffusivity decreased linearly in six hours. This indicated that the weight change was more sensitive to oxidation than the thermal diffusivity.

Figure 6 shows the relation between the thermal diffusivity and weight change of 3D C/SiC and the oxidation time at 600°C. The weight loss also accelerated parabolically with increasing oxidation time. The corresponding thermal diffusivity decreased very slowly in six hours, indicating that the weight change was much more sensitive to oxidation than the thermal diffusivity.

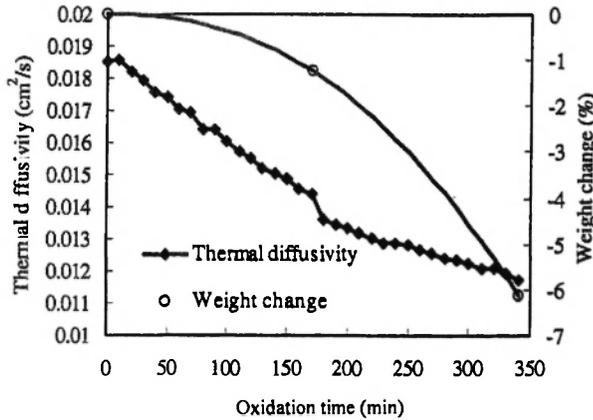


Fig. 5: Thermal diffusivity and weight change of 2D C/SiC against oxidation time at 600°C

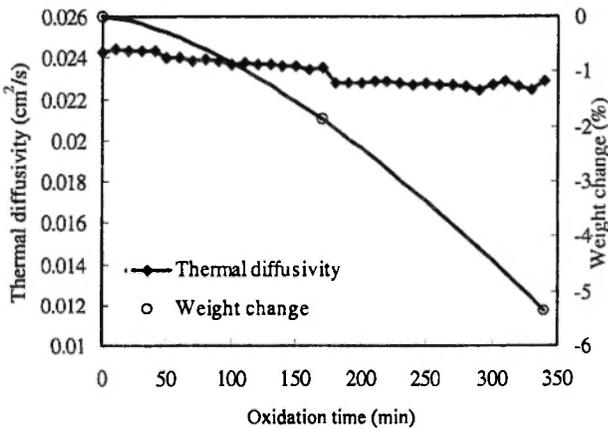


Fig. 6: Thermal diffusivity and weight change of 3D C/SiC against oxidation time at 600°C

Because thermal diffusivity of the interfacial gaps produced by oxidation of the carbon phase can be neglected, the thermal diffusivity of the C/SiC composites can be expressed as

$$\alpha_{CS}^n = \alpha_C^n (V_C - V) + \alpha_S^n (1 - V_C) \quad (1)$$

where α_{CS} , α_C and α_S are the thermal diffusivity of the C/SiC, the carbon phase and the SiC matrix, respectively, V_C is the initial volume fraction of the carbon phase, V is the fraction of the oxidized carbon phase, and n is an index that reflects the mixing manner of the carbon phase and the SiC matrix. For any two-phase material, the maximum value of n is +1, showing that

the two phases are parallel to each other and the thermal flow direction, and the minimum value is -1, showing that the two phases are parallel to each other and perpendicular to the thermal flow direction.

The fraction of the oxidized carbon phase can be related to the oxidation time by

$$V = \frac{At^{n'}}{\rho C} \quad (2)$$

where A is a constant, n' is an index, and ρC is the density of the carbon phase. If α_{CS} were considered to decrease linearly with oxidation time, then n should be the reciprocal of n' . As a result, the value of n for 2D C/SiC was calculated to be 0.43, and that for the 3D C/SiC to be 0.66. This shows that the network of SiC matrix deposited in 3D performs is more uniform than that in 2D performs.

3.3. Thermal diffusivity and weight change at 1300°C

The relation between the thermal diffusivity and weight change of 2D C/SiC and the oxidation time at 1300°C is shown in Fig. 7, and that of 3D C/SiC is shown in Fig. 8. In contrast with the weight losses of the two composites at 600°C, they decelerated parabolically with increasing oxidation time at 1300°C owing to the formation of silica. Although the weight loss of 3D

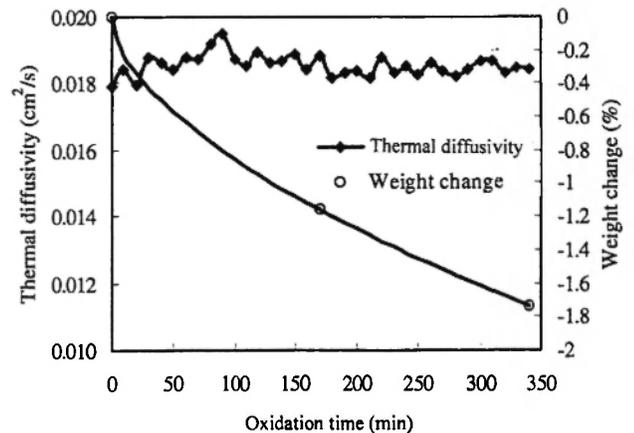


Fig. 7: Thermal diffusivity and weight change of 2D C/SiC against oxidation time at 1300°C

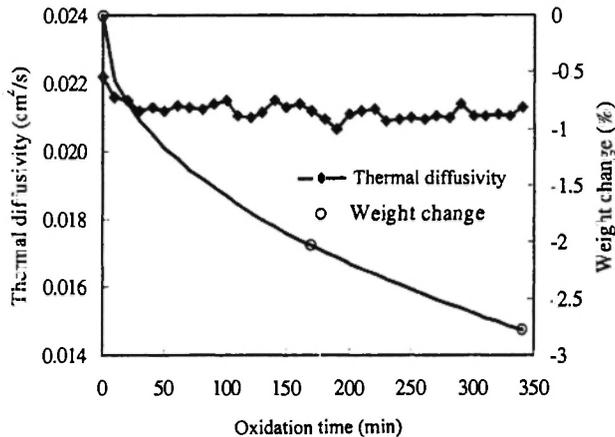


Fig. 8: Thermal diffusivity and weight change of 3D C/SiC against oxidation time at 1300°C

C/SiC was greater than that of 2D C/SiC, the corresponding thermal diffusivity of 3D C/SiC was still maintained in six hours like that of 2D C/SiC. It can be confirmed that non-uniform oxidation took place and no interfacial gaps were formed between the carbon phase and the SiC matrix. It is not difficult to understand that the weight loss of C/SiC composites produced by uniform oxidation is less favorable to their thermal diffusivity than that produced by non-uniform oxidation.

The SiC matrix was deposited differently in the two kinds of performs with different pores and it was the controlling constituent that led to different thermal diffusivity of the composites. It cannot be used as a property for evaluating damage of the composites in service.

4. CONCLUSIONS

1. The thermal diffusivity of 2D C/SiC was greater than that of 3D C/SiC over the entire temperature range. The former was more sensitive to oxidation than the latter. Below 1000°C, the thermal diffusivity of 2D C/SiC decreased with increasing oxidation time. The lower the temperature, the more rapidly it decreased.
2. The thermal diffusivity of 3D C/SiC did not decrease significantly with increasing oxidation time in the whole temperature range. At 600°C, the

weight loss of both composites accelerated parabolically as a function of oxidation time, but their thermal diffusivity decreased linearly.

3. At 1300°C, the weight loss of both composites decelerated parabolically as a function of oxidation time, but no obvious thermal diffusivity change corresponded to the weight loss. Oxidation had a much stronger effect on the weight loss than on the thermal diffusivity of C/SiC composites.

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